Thin $Cu(InGa)Se_2$ Solar Cells

Bill Shafarman
Institute of Energy Conversion

Outline

A. Introduction: What is "thin"?

B. Review experimental results in literature

C. IEC results: compare etched and thin deposited films

D. Back contact

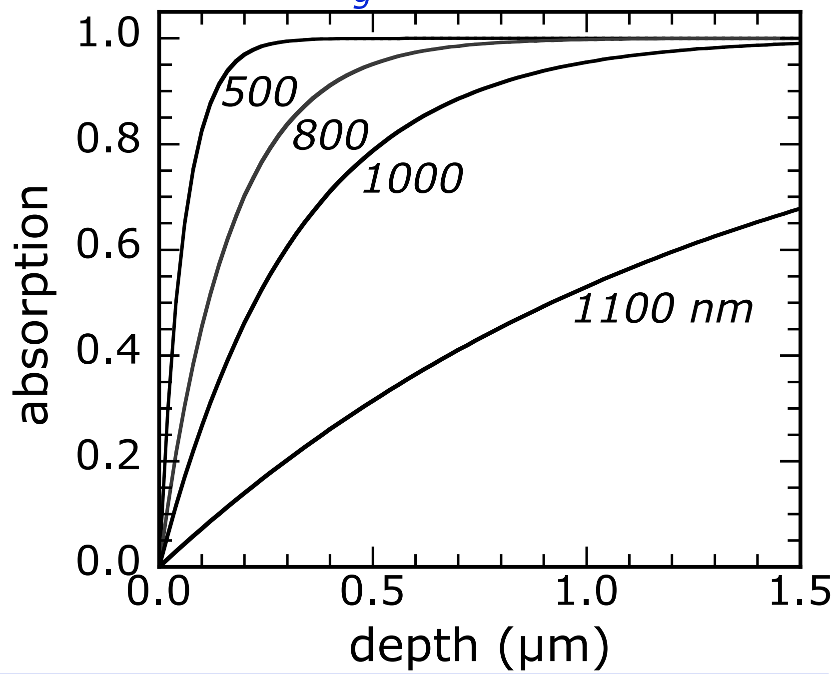
E. Light trapping

Introduction

What is "thin"? Consider relevant lengths:

- Typical absorber layer thickness (d)
  - 1.5 – 3 μm in laboratory cells
  - 1.2 – 1.5 μm in production modules
- Electronic lengths
  - Minority carrier diffusion length 0.1 < L < 1 μm
  - Space charge width w ≤ 0.5 μm
- Optical absorption depth depends on wavelength
- So, let's say "Thin" means < 1 μm, Goal could be 0.5 μm

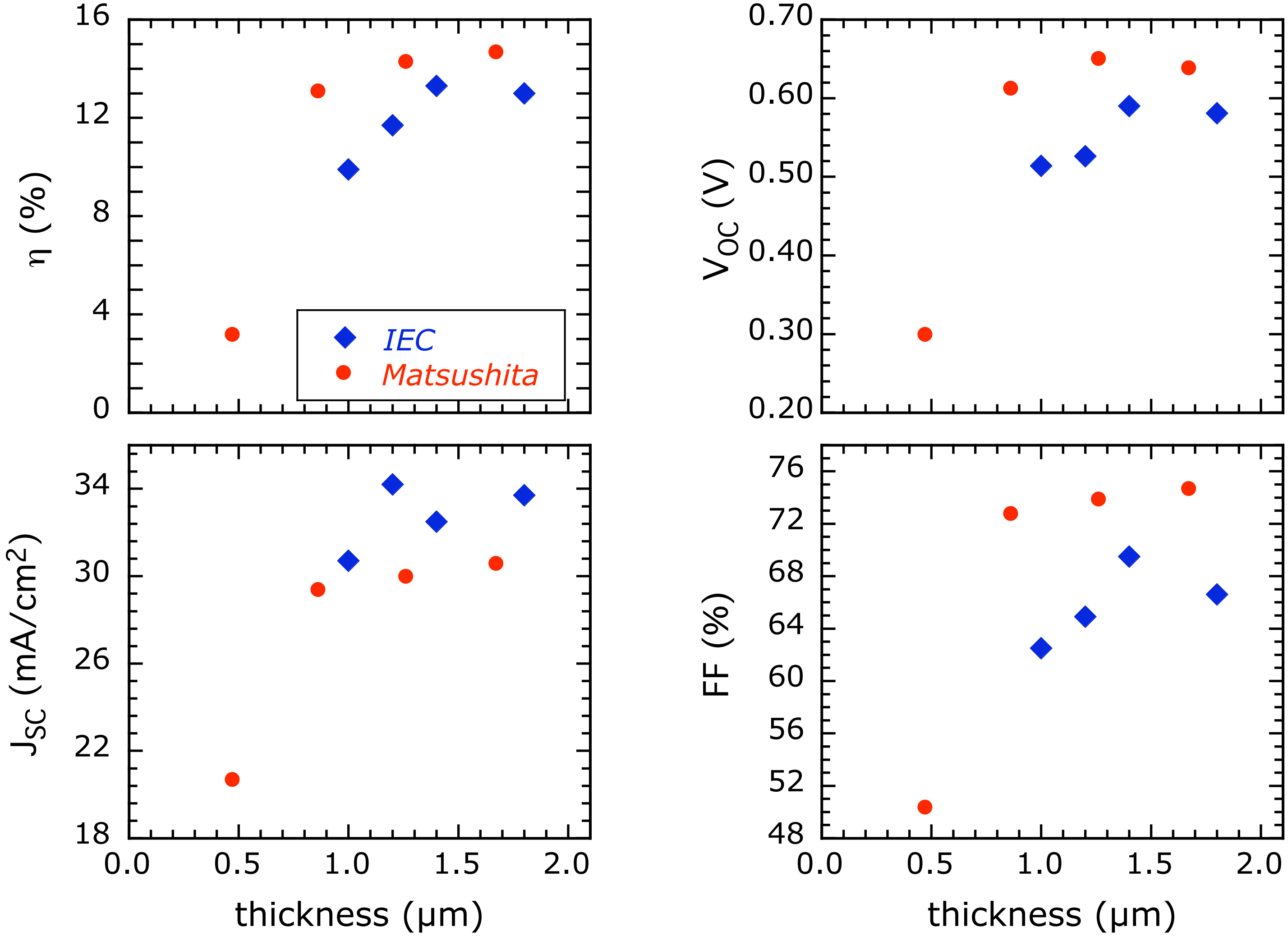
E_g = 1.15 eV



Review Laboratory Cell Results

1. Bi-layer evaporation (Cu-rich / Cu-free) - IEC
   Shafarman, et.al. *Proc, 26th IEEE PVSC,* 331 (1996)
   - Uniform bandgap through film
2. Three-stage evaporation - Matsushita
   Negami, et.al. *Proc.2nd WCPEC*, 1181 (1998)
   - Ga gradient from back to front, large grain size
3. Simulated in-line evaporation - ÅSC (Uppsala)
   Lundberg, et.al. *Prog. Photov.* **11**, 77 (2003)

Review Laboratory Cell Results

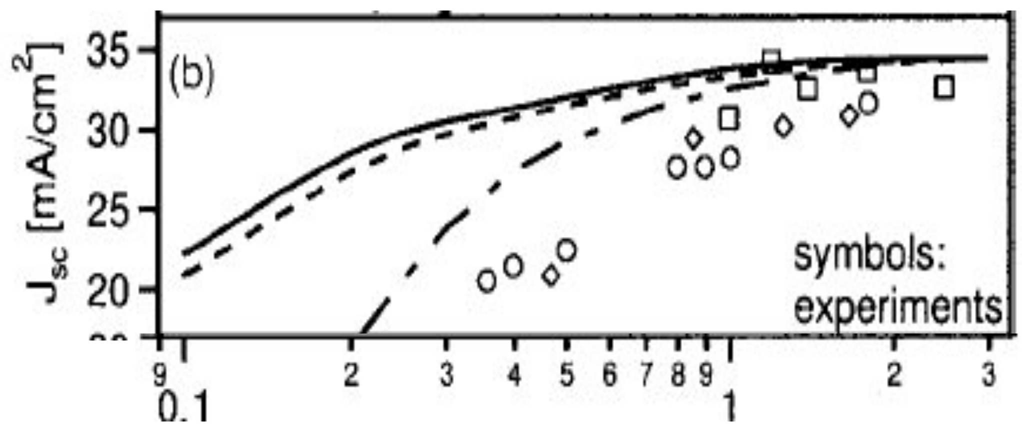


Review Laboratory Cell Results

General trends and observations

- Both IEC and Matsushita results limited by shunting of cells for d ≤ 1 µm - need to control film roughness?
- Decrease in J_{SC}
  - expected for d < 1 µm due to incomplete absorption

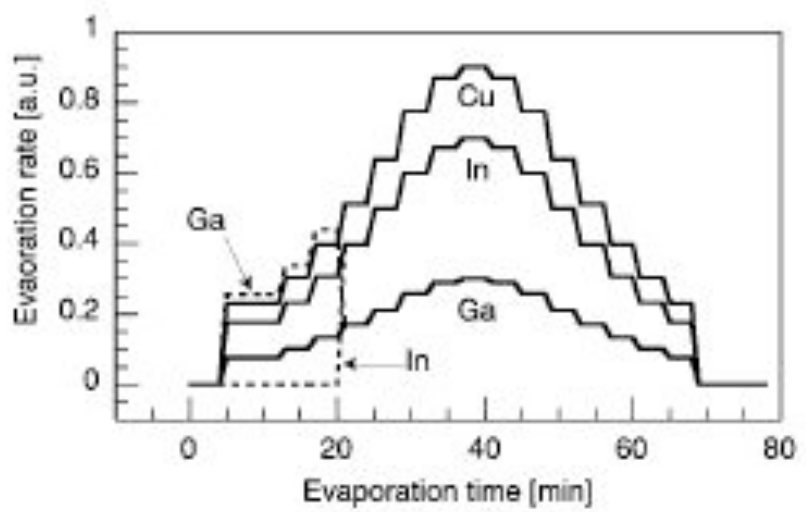
    Gloeckler and Sites, *J. Appl. Phys.* **98**, 103713 (2005)



ÅSC Results

Compare films with:

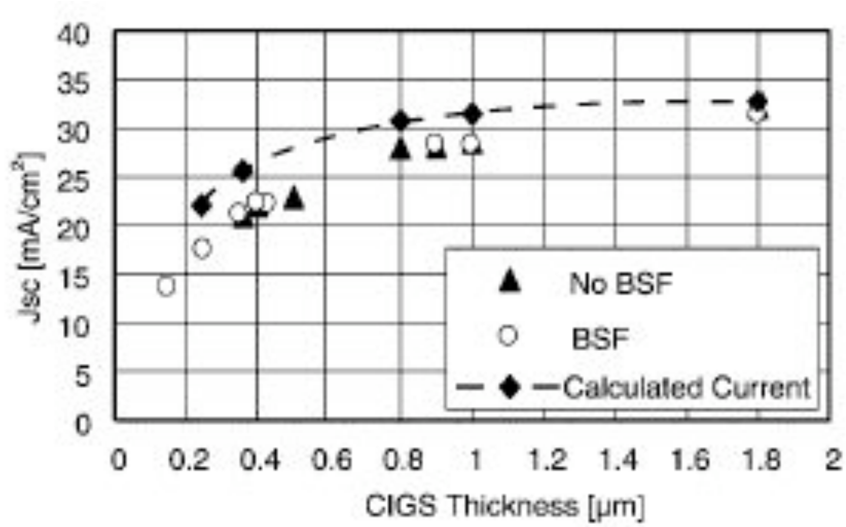
- uniform bandgap through-film
- $CuGaSe_2$ layer at back of film to provide a back surface field (BSF)
  - provide barrier to electrons, reduce recombination at back contact



Cell Results: ÅSC - J_{SC}

J_{SC} decrease with reduced thickness

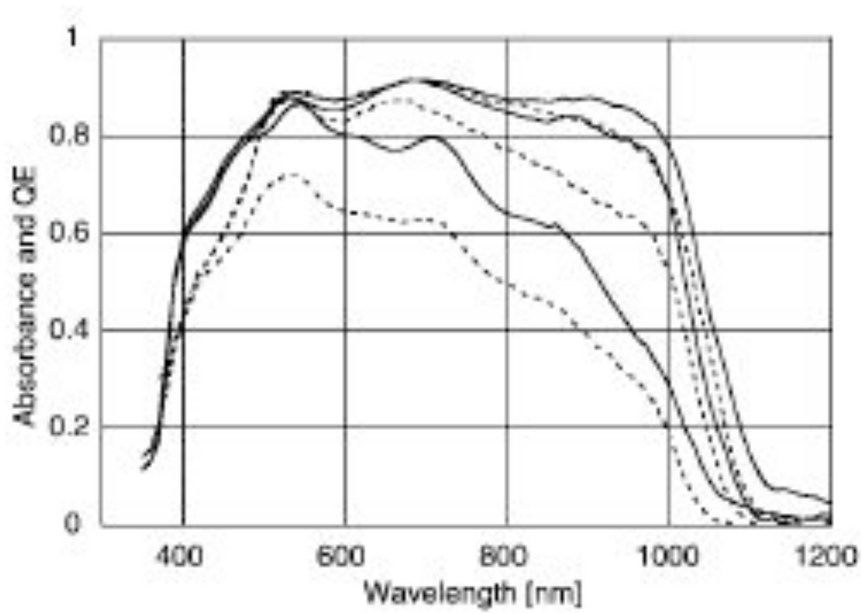
- With d < 1 μm J_{SC} decrease is greater than predicted by model based on optical absorption
- No improvement with high Ga BSF



Cell Results: ÅSC - J_{SC}

Calculated loss in J_{SC}

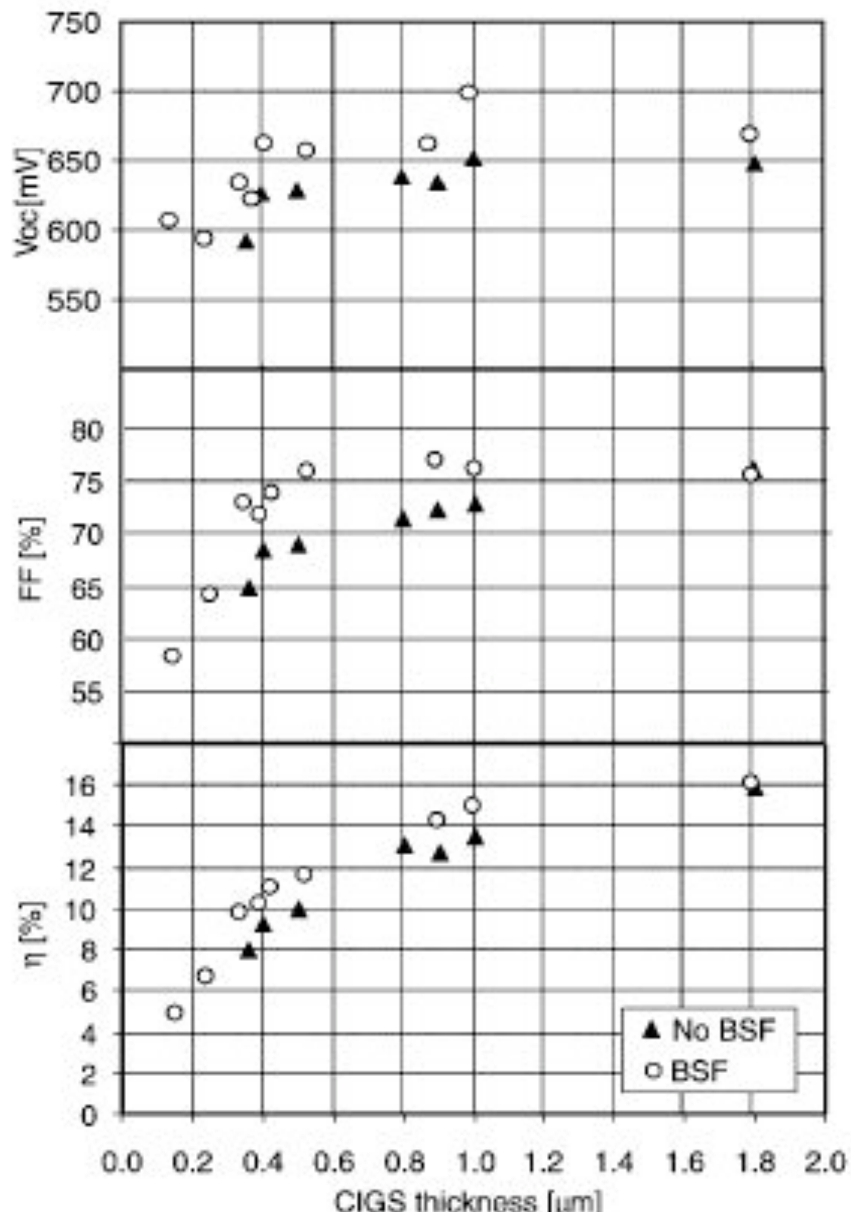
- Compare calculated QE based on optical absorption (solid) and the measured QE for $Cu(InGa)Se_2$ thicknesses of 1.8, 0.8 and 0.36 mm



Cell Results: ÅSC

The other
J-V parameters

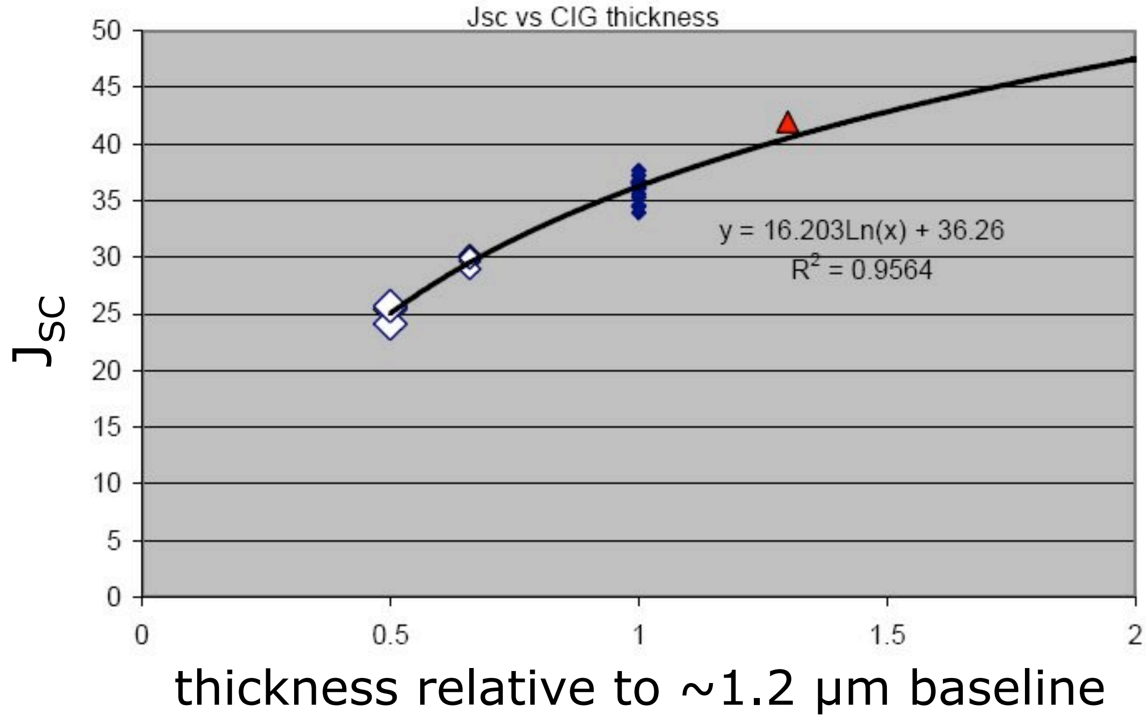
- V_{OC} decrease for d < 0.5 µm
  - higher with BSF at all thicknesses
- FF decrease for d < 1 µm
  - for d< 0.5 µm with BSF
  - field aided collection?
- η decreases for d < 1 µm but BSF improves η at all thicknesses



Shell Solar Results

Baseline process

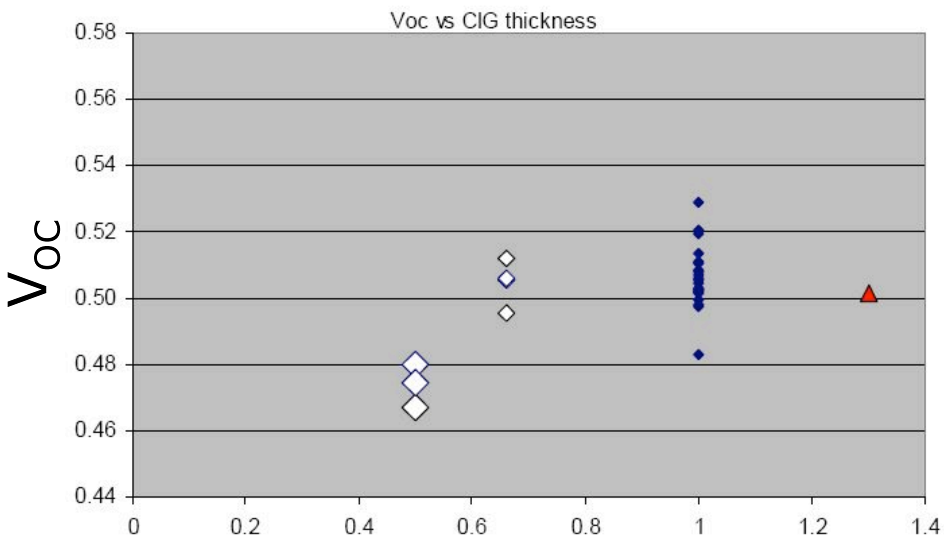
- Deposition by reaction of metal precursor films
- Baseline thickness ≈ 1.2 μm
- Unpublished results, provided by Dale Tarrant



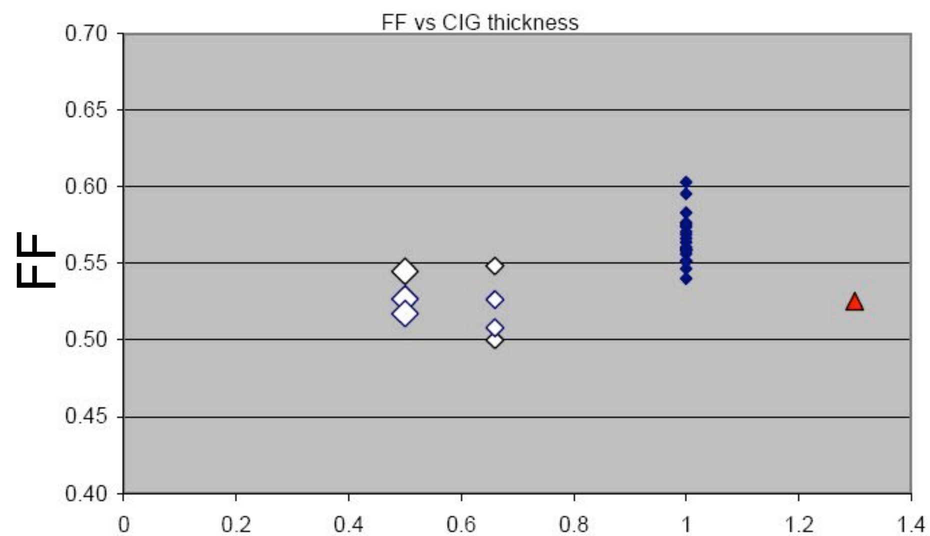
Shell Solar Results

High yield manufacturing process ⇒ behavior is comparable to results with evaporated films

- J_{SC} decrease for d ≤ 1 µm
- V_{OC} decrease at d = 0.6 µm , note Ga gradient ~ BSF
- FF independent of d



thickness relative to ~1.2 µm baseline



thickness relative to ~1.2 µm baseline

New IEC results

Evaporated $Cu(InGa)Se_2$

- Uniform layer deposition
  - easily scalable: thickness $\propto$ time
  - through-film composition is constant (AES)
  - more dense films $\Rightarrow$ minimize shunt formation?
- Etched films
  - smoothing etch starting from 2 μm thick baseline films
  - very smooth, specular surface
  - controlled reduction in thickness
  - potential to better quantify optical losses

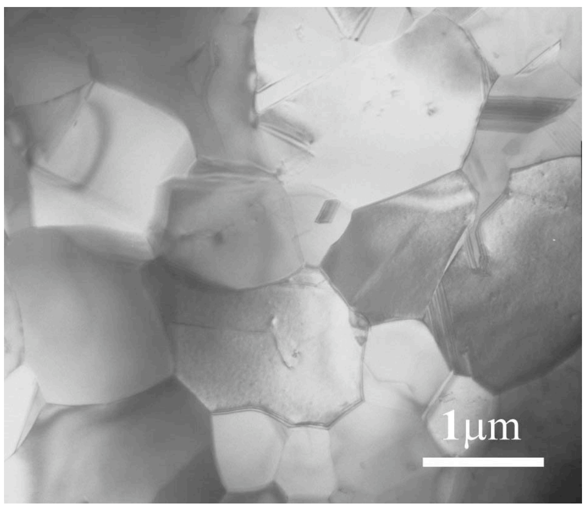
CIGS morphology

TEM images show voids in films grown with 2-step process but not in films grown with uniform evaporation.

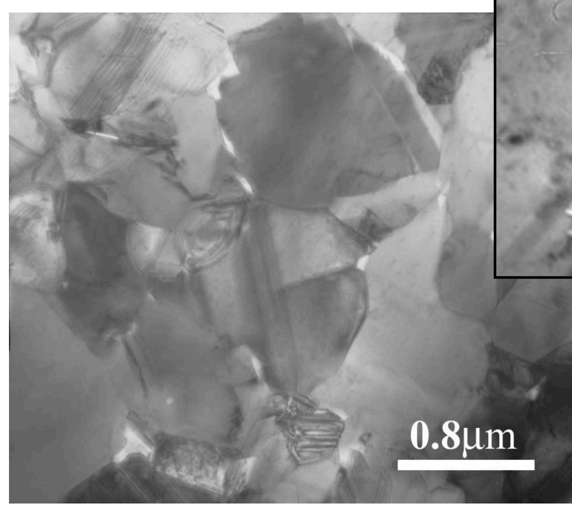
Lei, Rockett and Robertson, Univ. of Illinois

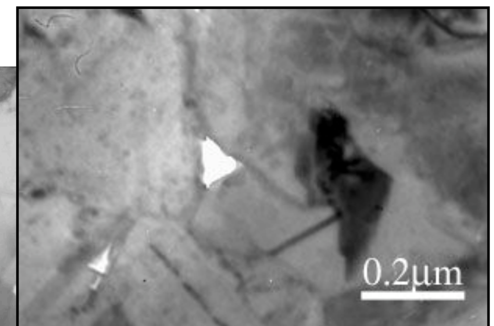
- Are voids cause of shunts in thin layers?

Uniform growth
(no Cu-rich stage)



Bi-layer growth
(Cu-rich/no Cu)





$Cu(InGa)Se_2$ Etch

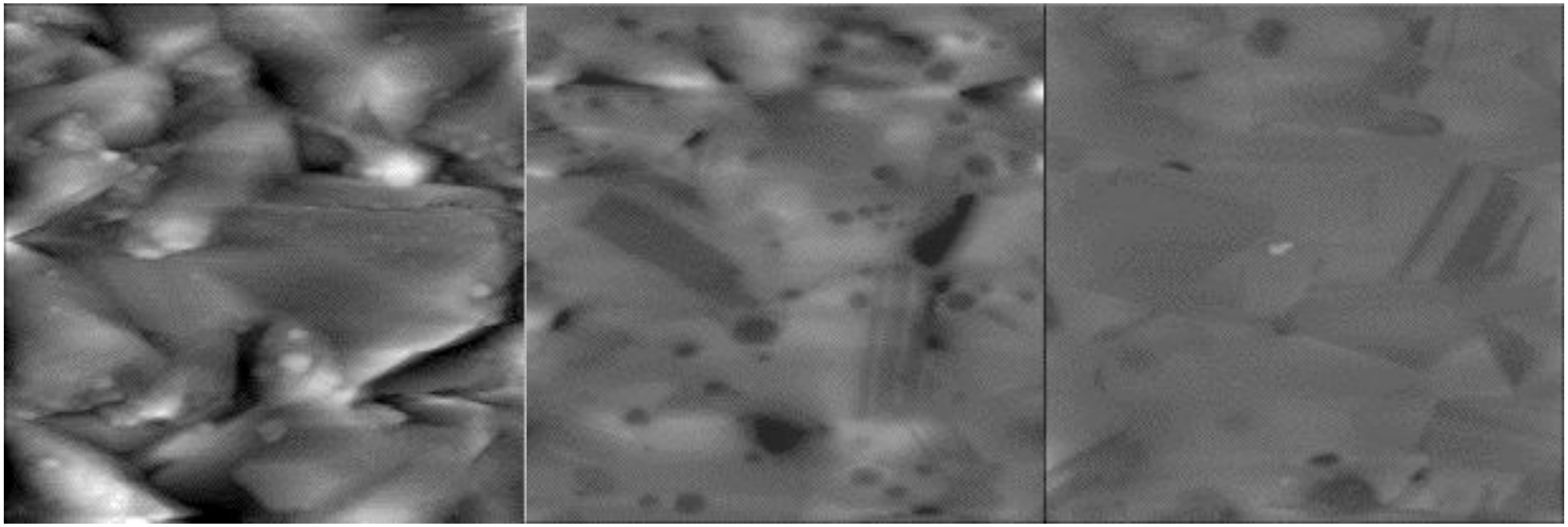
- Aqueous Br-etch smoothes $Cu(InGa)Se_2$ surface
  Birkmire, McCandless, *Appl. Phys. Lett.* **53**, 140 (1988)
- Residual Se on surface must be removed to make devices
  Canava, et.al. *J. Phys. Chem. Sol.* **64**, 1791, (2003)
  - KCN etch
  - vacuum anneal (250°C, 10 min)
- Characterize roughness by surface area difference
  $\Delta A_{surf} = (A_{surf} - A_{im})/A_{im}$

$Cu(InGa)Se_2$	ΔA_{surf}
As-deposited (550°C)	19 %
Br-etch	3 %
KCN etch	1 %

- Use etch to:
  - Smooth surface used for optical characterization of $Cu(InGa)Se_2$ and buffer layers
  - Controlled reduction in $Cu(InGa)Se_2$ thickness

Cu(InGa)Se_2 Etch

As-deposited | Br-etch | KCN etch



52 nm | 21 nm | 8 nm

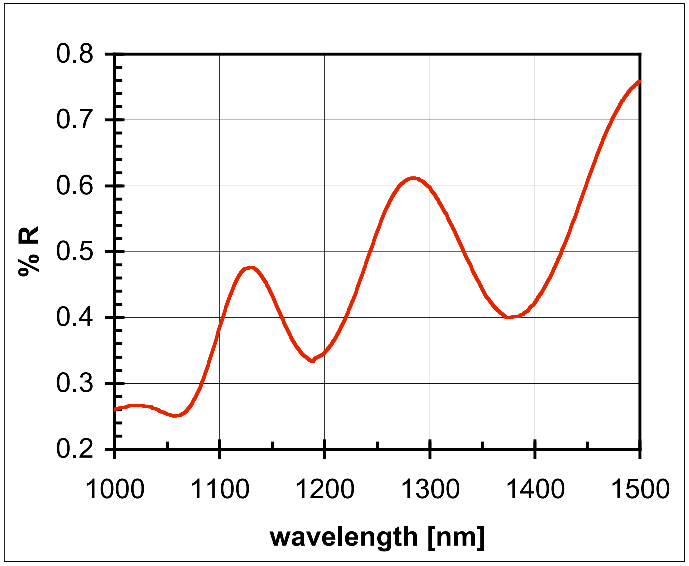
rms roughness

Thickness measurement

Determine thickness from interference fringes in reflection spectrum Swanepoel, *J. Phys. E* **16**, 1214 (1983)

- Need n vs. λ Paulson, et.al., *J. Appl. Phys.* **94**, 879 (2003)

$$2nd = m\lambda \qquad d = \frac{\lambda_1 \lambda_2}{2\left(\lambda_1 n_2 - \lambda_2 n_1\right)}$$



Minima

λ1	n1	λ2	n2	λ3	n3	d1	d2
1057	**3.032**	**1187**	**2.92**	**1380**	**2.863**	1224	1298

Maxima

λ1	n1	λ2	n2	λ3	n3	d1	d2
1025	**3.055**	**1130**	**3.054**	**1283**	**2.884**	1800	1099

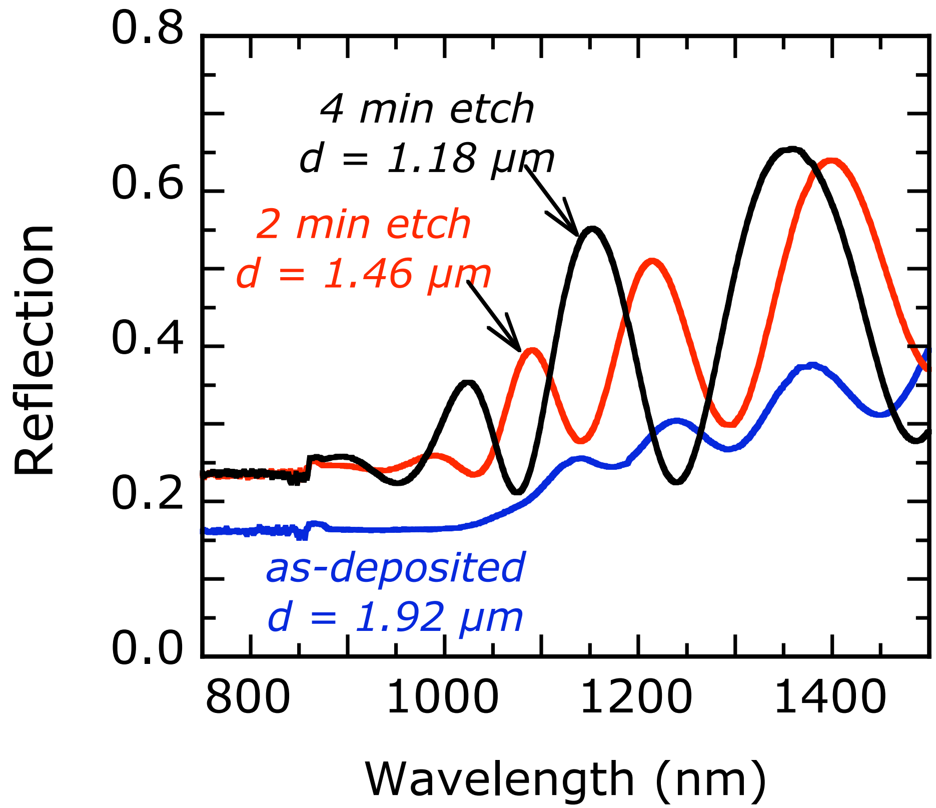
d avg	**1355**
stdev	**307**

	λ	n	m(est)	m(exact)	d new
Maxima	1025	3.055	8.1	**8**	1342
	1130	3.054	7.2	**7**	1295
	1283	2.884	6.1	**6**	1335
Minima	1057	3.032	7.6	**7.5**	1307
	1187	2.92	6.7	**6.5**	1321
	1380	2.863	5.6	**5.5**	1326
				d avg	**1321**
				stdev	**17**

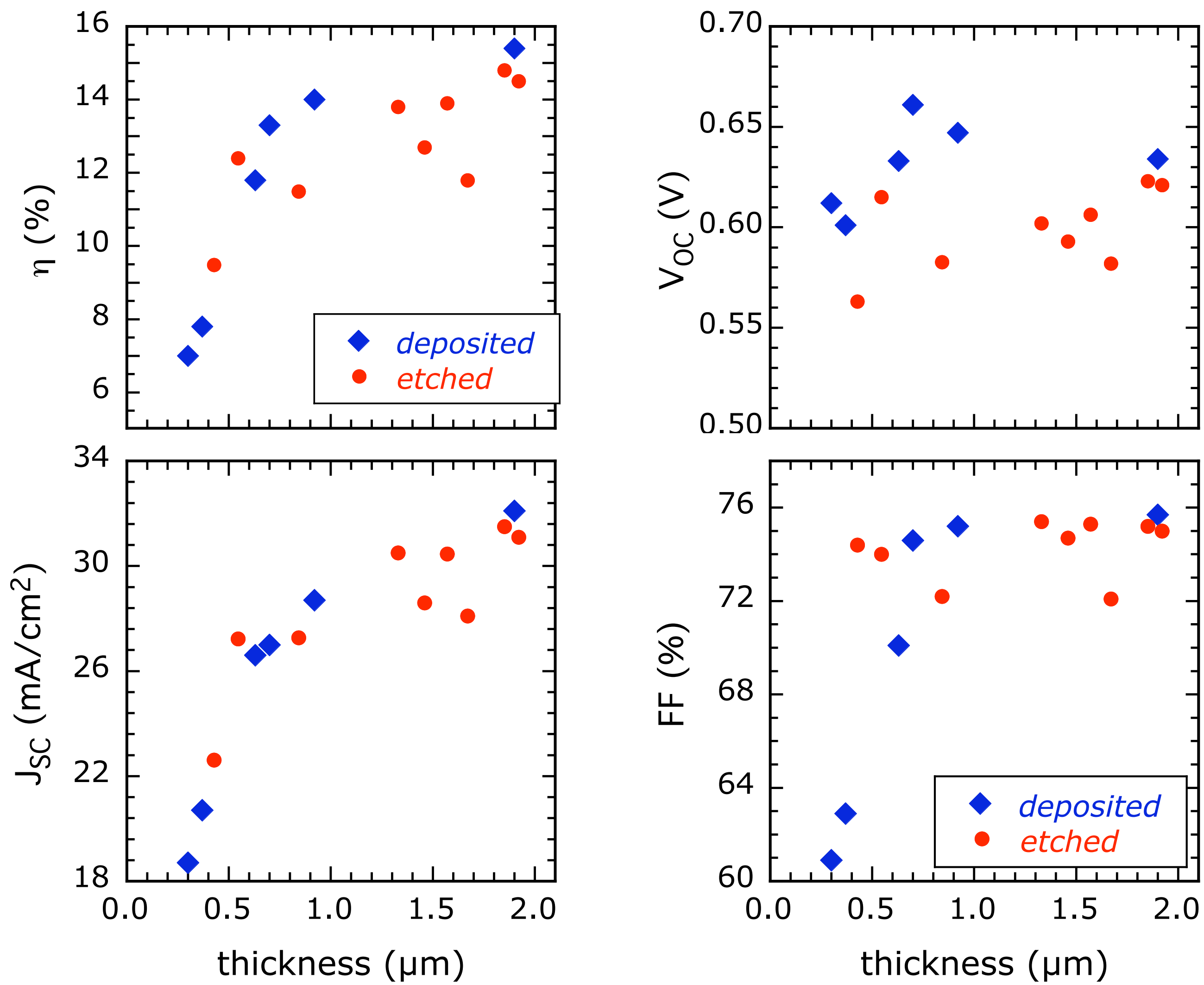
$Cu(InGa)Se_2$ Reflection

Effect of etch

- higher R in absorbing region ⇒ lower J_{SC} in devices
- greater interference effect due to specular surface

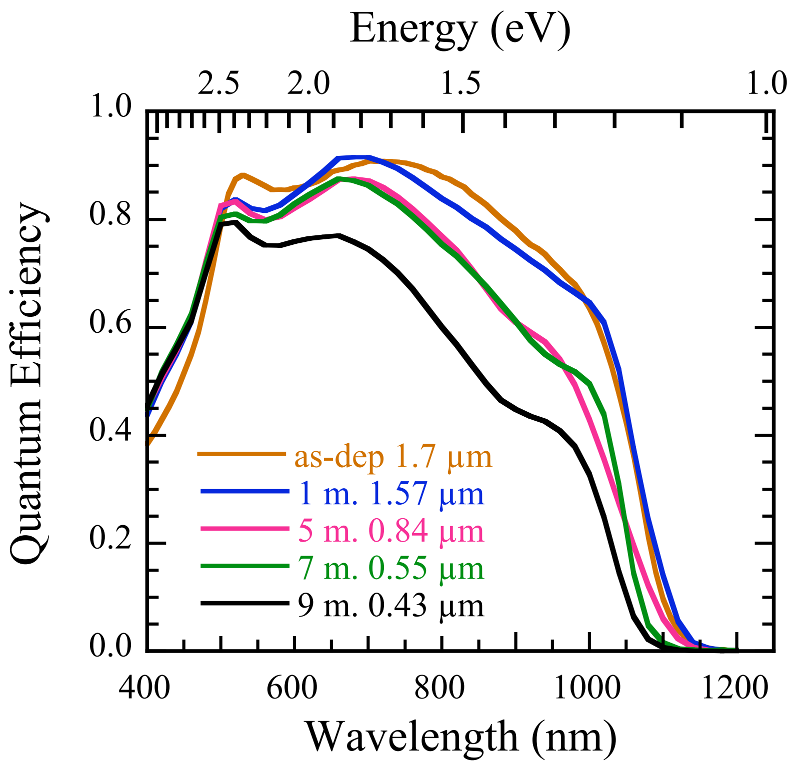


Cell results: deposition time vs. etch

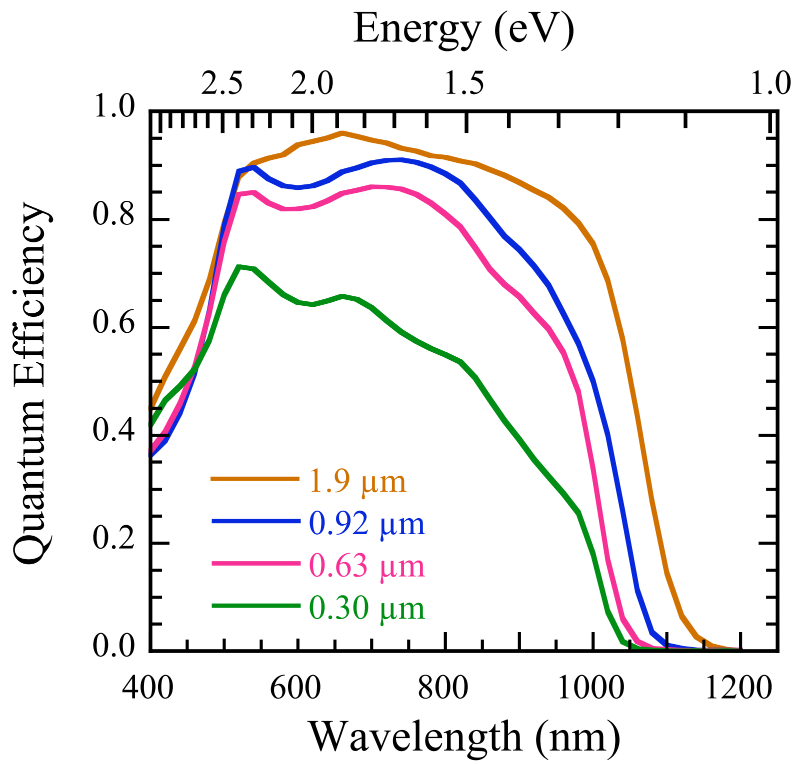


Cell results: deposition time vs. etch

Etched $Cu(InGa)Se_2$



Deposited $Cu(InGa)Se_2$



Cell results: shunting

Thickness varied with deposition time of uniform process

- For each time: 12 cells, 0.5 cm^2
- Yield reduced with thinnest layers due to shunts

d (μm)	Cells	η (%)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	G_{SC} (mS/cm^2)
1.90	best	15.4	0.634	32.1	75.7	0
	*average**	*14.3*	*0.628*	*31.5*	*72.1*	*2*
0.92	best	14.0	0.647	28.7	75.2	0
	*average**	*12.9*	*0.640*	*28.3*	*71.1*	*1*
0.70	best	13.3	0.661	27.0	74.6	1
	*average**	*12.5*	*0.663*	*26.2*	*72.0*	*1*
0.63	best	11.8	0.633	26.6	70.1	1
	*average**	*9.8*	*0.617*	*25.3*	*62.8*	*3*
0.30	best	7.0	0.612	18.7	60.9	3
	*average**	*3.9*	*0.5*	*18.6*	*41.5*	*25*

* out of 12 cells on 2 pieces

$G_{SC} \equiv dJ/dV(V=0)$

Cell results: deposition time vs. etch

- Loss of J_{SC} with decreasing d similar to previous results
- Scatter in V_{OC}, apparent decrease only for d < 0.5 μm
- High FF ~ 75% at d = 0.43 μm with etched cells
  - all other cells without BSF showed decreasing FF
- Uniform process, dense films may reduce shunting

Discussion of cell results

Loss of J_{SC} always greater than predicted from optical absorption.

What are possible causes?

- Incomplete current collection
  - may be due to poor material quality at back of $Cu(InGa)Se_2$
  - but high FF suggests that collection is not the problem
- Reflection loss at back contact
  - but Gloekler and Sites model didn't fit data even with $R_b = 0$
- Recombination at back surface
  - but BSF didn't increase current
- Are the models missing something?

And what are paths for improvement?

- More reflective back contact
- Light scattering to increase optical path length in absorber

Discussion of cell results (cont.)

FF and Voc

- In best cases, constant for d ≥ 0.4 µm
  - ÅSC cells with BSF, IEC cells with etched $Cu(InGa)Se_2$
- Effect of back surface recombination,
  - role of back surface field is not clear

Back Contact Reflector

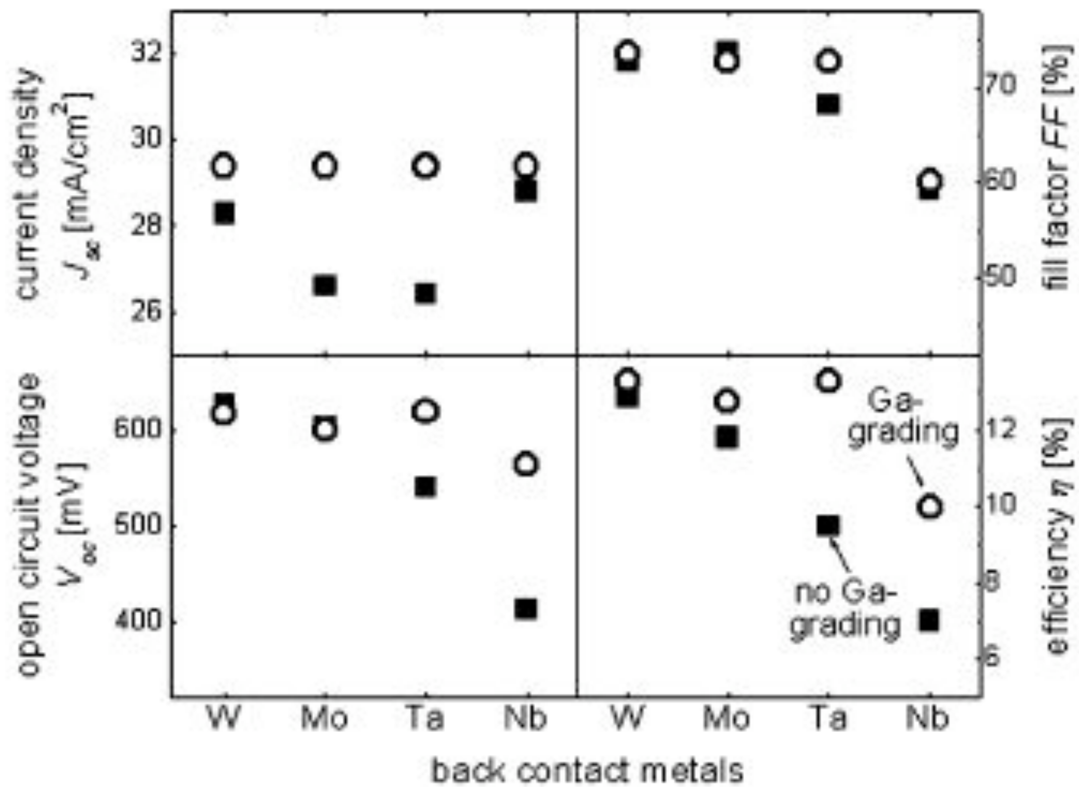
Alternative metals can provide improved reflection

- Selection criteria:
  - low cost
  - expected high reflection
  - tolerance to Se reaction - rules out Ag or Al
- Experimental comparison of W, Ta, Nb, and Mo
  Orgassa, et.al. Thin Sol Films 431, 387 (2003)
  - expected improvement in J_{SC} for Nb, Ta not obtained
    - varying surface roughness effects comparison
  - also tried Cr, V, Ti, and Mn but films reacted with Se
  - Good cell performance with W and Ta
    - back surface field (Ga gradient) needed for Ta, Nb

Back Contact Reflector

Results from Orgassa et.al.

Metal	Mo	W	Ta	Nb	Cr
η (%)	13.8	14.2	13.3	10.0	5.9

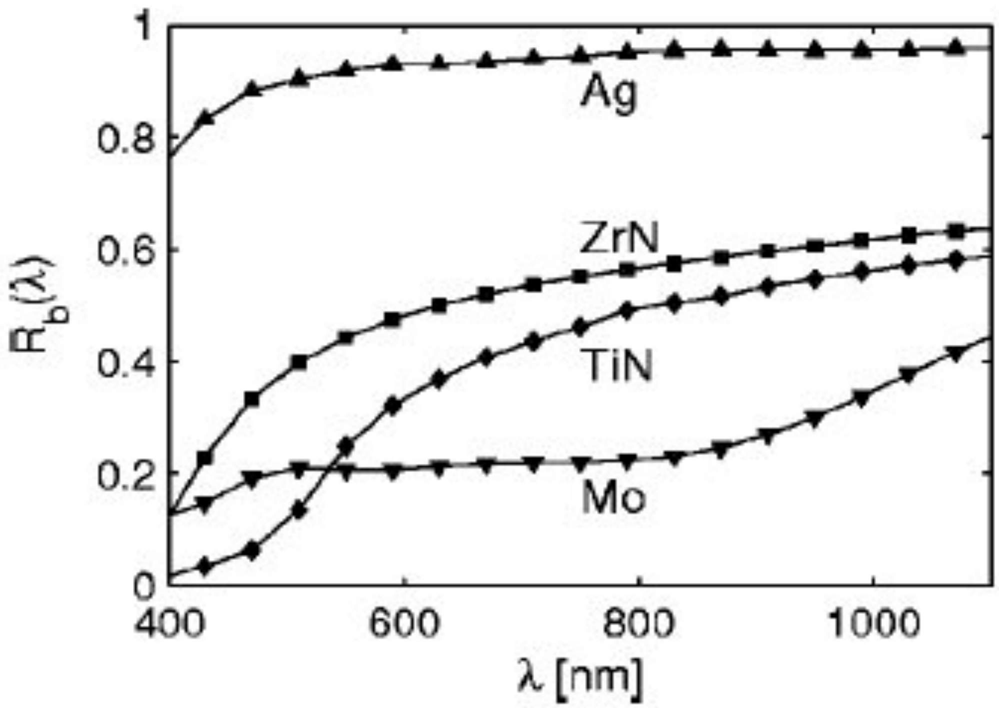


Back Contact Reflector

Other back contacts: TiN and ZrN

- Stable in high temperature Se environment
- Calculated reflection at $Cu(InGa)Se_2$/contact interface

Malmström, et.al. *Appl. Phys. Lett*. **85**, 2634 (2004)

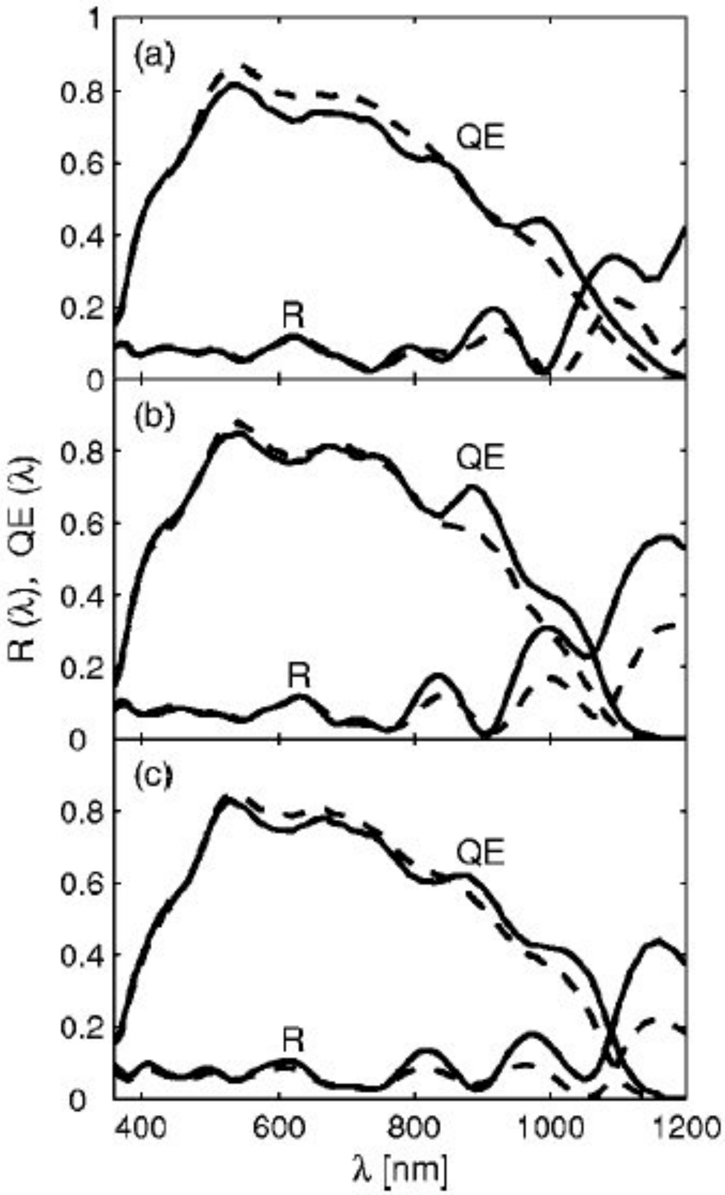


Back Contact Reflector

- TiN cell results   Malmström, et.al. *3rd WCPEC*, 344 (2003)
  - $\eta \approx$ 13% using 0.5 μm $Cu(InGa)Se_2$
- ZrN cell results with 0.6 μm $Cu(InGa)Se_2$
  - Low V_{OC} and FF with Mo/ZrN contact
  - Improved V_{OC} with Ga gradient or $MoSe_2$ layer
  - Small increase in long wavelength QE

Back contact	η (%)	V_{OC} (V)	J_{SC} (mA/cm2)	FF (%)
Mo	9.7	0.535	25.0	72.5
Mo/ZrN	7.2	0.456	24.9	62.8
Mo/Ga grade	11.4	0.637	25.5	70.9
Mo/ZrN/Ga grade	10.2	0.572	26.9	66.0
$Mo/MoSe_2$	9.2	0.518	25.5	69.8
$Mo/ZrN/MoSe_2$	10.4	0.580	25.4	70.5

ZrN Contact



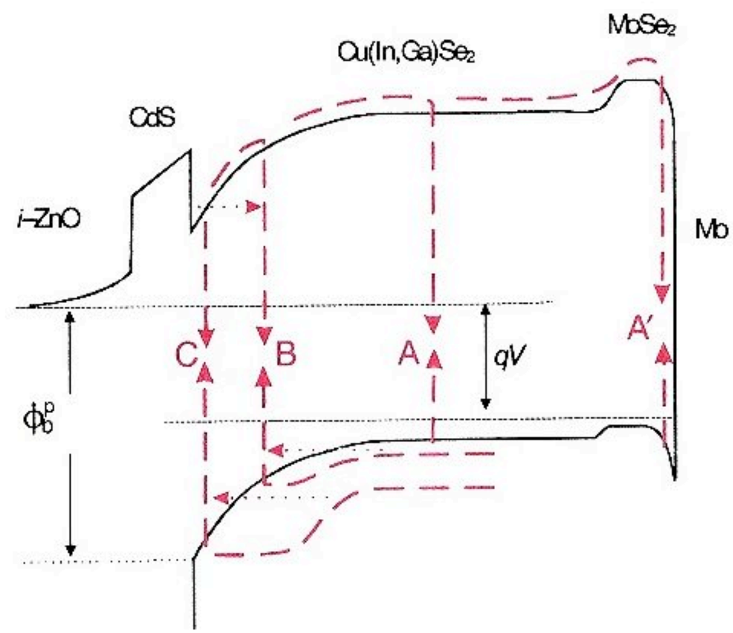
With Ga gradient in $Cu(InGa)Se_2$

With $MoSe_2$ layer

Malmström, et.al. *Appl. Phys. Lett*. **85**, 2634 (2004)

Understanding the Back Contact

- With Mo can assume that $MoSe_2$ layer is always formed
  Wada, et.al., *Jap. J. Appl. Phys* **35**, L1253 (1996)
- Back surface field formed by high Ga layer
  - not necessary to maintain V_{OC} with Mo contact
  - increases V_{OC} with alternate contacts
- $MoSe_2$ layer increases V_{OC} with ZrN contact
- Suggest that $MoSe_2$ forms BSF
  - $E_g(MoSe_2)$ = 1.4 eV
  - suggested by Rau and Schock

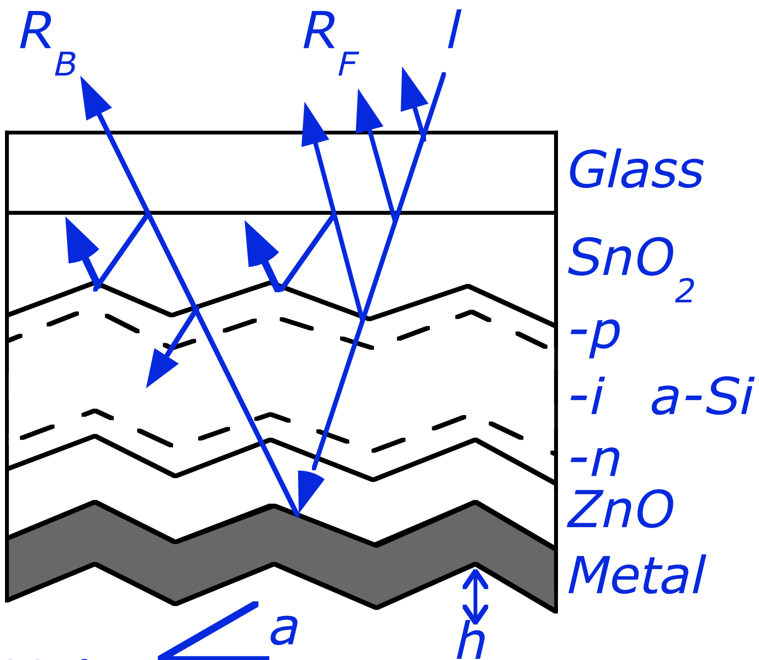


Rau and Schock, *in Clean Electricity from Photovoltaics, ed. M. D. Archer and R. Hill*, (2001)

Light Trapping

Used extensively in a-Si solar cells

- Best cells use combination of back reflector and optimized light scattering to increase optical path length
  - ZnO/Ag or ZnO/Al reflector
  - Textured ZnO or SnO_2
- Detailed optical models have been developed

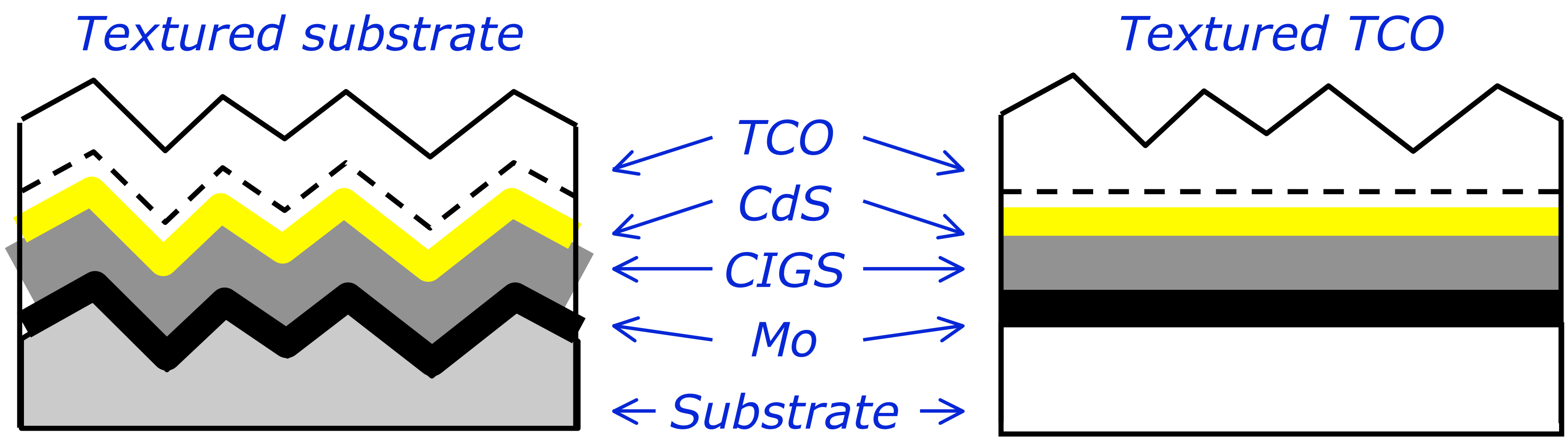


Lablanc et.al. *J. Appl Phys* 75, 1074 (1994).
Hishikawa et.al. *Sol. Energy Sol. Cell Mat.* 49,143 (1997)
Hegedus and Kaplan, *Prog in Photov.* 10, 257 (2002).

Light Trapping in $Cu(InGa)Se_2$

Can provide texture at top or bottom of cell

- Textured substrate, e.g. metal foil or textured film on substrate
  - assess conformality of subsequent layers
- Textured ZnO or ITO

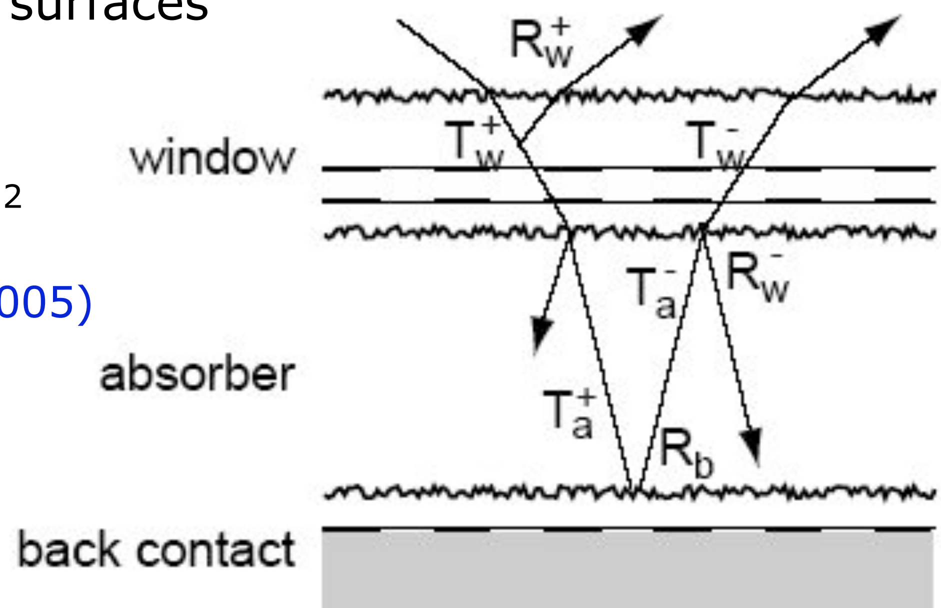


Light Trapping in $Cu(InGa)Se_2$

Models of effect of light scattering in $Cu(InGa)Se_2$ cells

- Increase in J_{SC} calculated for Ag reflector with 0.5 µm absorber
  Malmström, et.al. *3rd WCPEC*, 344 (2003)
  - 2.0 mA/cm^2 with specular surfaces
  - 3.5 mA/cm^2 with scattering surfaces

- Effect of measured $Cu(InGa)Se_2$ surface roughness
  Krc et.al., *20th EuroPSEC*, 1831 (2005)
  - Not enough to fit measured QE



Conclusion: Some Critical Questions

- Why is J_{SC} so low?
  - Do we need better optical models?
  - Is there a confirmation of improved J_{SC} (and long λ QE) with a better back reflector?
- What is the role of the $MoSe_2$ layer in creating a back surface field and in optical reflection?
  - band alignments between $Mo/MoSe_2/Cu(InGa)Se_2$
- Does film growth need to be optimized for thin layers:
  - control morphology with changing d
  - may be tradeoff between texture for light scattering and shunting
  - control nucleation to ensure quality material at back
- Best designs for back contact, BSF, light scattering